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(19)



(54) METHOD OF STABILIZING ACID AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE

(71) We, TOKAI DENKA KOGYO KABUSHIKI KAISHA, a Japanese company, located at Room 428, Ohtemachi Buildings, 6-1, 1-Chome Ohtemachi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relate to a method of stabilizing acidic aqueous solutions of hydrogen peroxide which are used in chemically solubilizing treatments such as pickling, etching and chemical polishing of copper and copper alloy. More particularly, it is an object of this invention to adding glycol ethers to acidic aqueous solutions of hydrogen peroxide being unstable in the presence of copper ions to inhibit decomposition of the hydrogen peroxide for achievement of its economical use.

Chemically dissolving treatments such as pickling, which is removal by dissolving of oxidation scales on the surface of metallic materials, etching, which is removed by dissolving of a portion of metallic phase and chemical polishing, which is polish treatment of the surface are utilized in a wide area of industrial fields involving metallic materials.

Acidic aqueous solutions of hydrogen peroxide are known to possess high solubilizing powers as a chemically solubilizing agent for copper and copper alloy materials. On the other hand, hydrogen peroxide is a readily decomposable compound which is catalytically decomposed especially in the presence of copper ion. Consequently, it is economically disadvantageous that when an acid aqueous solution of hydrogen peroxide is employed in the chemically solubilizing treatment of copper and copper alloy the copper is dissolved and accumulated in the solution to accelerate decomposition of the hydrogen peroxide thereby considerably lowering the ratio of effective utilization of hydrogen peroxide.

Typical solutions among the acidic aqueous solution for use in the chemically solubilizing

treatment of copper and copper alloy contain 10—150 g./l. of hydrogen peroxide and 10—200 g./l. of sulfuric acid. These solutions have been critically defective in practical uses in that, whereas they are stable in the absence of copper ion therein, the hydrogen peroxide will be rapidly decomposed or disappear in the presence of copper ions accumulated in the solutions.

Known methods for reducing the decomposition of hydrogen peroxide comprise adding as a stabilizer saturated aliphatic alcohols, phenols, proteins or polymethylene polyamines in the said aqueous solution of hydrogen peroxide. But, stabilizers having a more improved stabilizing property have been desired.

We have found that glycol ethers have extremely excellent effects for stabilizing hydrogen peroxide in an acidic aqueous solution of hydrogen peroxide and are very advantageous stabilizers of practical use.

This invention, on the basis of this finding, provides a stabilizing method superior to any of the heretofore known methods of stabilization.

According to the present invention there is provided a method of stabilizing hydrogen peroxide in an acidic aqueous solution of hydrogen peroxide containing copper ion capable of catalytically decomposing hydrogen peroxide, said method comprising adding as stabilizer to said aqueous solution, at least one glycol ether represented by the general formula



wherein R is an alkyl group containing 1 to 4 carbon atoms and n is 1 or 2.

Preferably, the aqueous solution contains a mineral acid, e.g. sulfuric acid. The use of sulfuric acid enables the stabilized solution to be used practically for the chemical solubilizing of copper and copper alloy.

In addition to sulfuric acid, the present invention is useful for acidic aqueous solutions of hydrogen peroxide containing another

mineral acid such as nitric or phosphoric acid.

The glycol ethers used in the invention are represented by the general formula



wherein R is alkyl containing 1—4 carbon atoms and n is 1 or 2. Examples are ethyleneglycol monomethylether, ethyleneglycol monoethylether, ethyleneglycol monobutylether, diethyleneglycol monomethylether, diethyleneglycol monoethylether and diethyleneglycol monobutylether.

Although these glycol ethers are more or less effective even at a concentration as low as 0.1 g./l. or lower, expected outstanding effects cannot be obtained at such a concen-

tration. The expected effects are obtained at a concentration higher than 0.1 g./l. and increase in the added amount leads to increase in the effect until it becomes approximately constant at 5 g./l. The addition more than 5 g./l. would be meaningless and uneconomical.

The invention will now be further illustrated by the following Examples.

Example 1.

To an aqueous solution containing 75 g./l. of H_2O_2 , 100 g./l. of H_2SO_4 and 50 g./l. of $CuSO_4 \cdot 5H_2O$ at $50^\circ C$ was added a glycol ether. Decomposed amounts of hydrogen peroxide were measured to give the results shown in the table below.

		Decomposed amount of hydrogen peroxide (mg.- H_2O_2 /l.min)	
Additive according to the invention		Added amount (g./l.)	
No additive		0	195
40	Ethyleneglycol monomethylether	0.1	54
	Ethyleneglycol monomethylether	0.5	13
	Ethyleneglycol monomethylether	1	5
	Ethyleneglycol monomethylether	5	1.8
45	Ethyleneglycol monomethylether	10	1.5
	Ethyleneglycol monoethylether	5	2.0
	Ethyleneglycol monobutylether	10	1.6
	Diethyleneglycol monomethylether	10	1.3
	Diethyleneglycol monoethylether	5	1.9
Diethyleneglycol monobutylether		20	1.4

Example 2.

Decomposed amount of the hydrogen peroxide in an aqueous solution containing 50 g./l. of H_2O_2 , 30 g./l. of HNO_3 , 50 g./l. of $CuSO_4 \cdot 5H_2O$ and 5 g./l. of ethyleneglycol monomethylether at $30^\circ C$ was 3 mg./1. min. Decomposed amount of the hydrogen peroxide in the absence of ethyleneglycol monomethylether added under the same conditions was 254 mg./1. min. It follows that the decomposed amount H_2O_2 was about 1/85 as much as the case without the addition.

Example 3.

Decomposed amount of hydrogen peroxide in an aqueous solution containing 100 g./l. of H_2O_2 , 50 g./l. of H_3PO_4 , 100 g./l. of $CuSO_4 \cdot 5H_2O$ and 5 g./l. of ethyleneglycol monobutylether at $60^\circ C$. was 2 mg./1. min. Decomposed amount of the hydrogen peroxide in the absence of ethyleneglycol monobutylether added under the same conditions was 221 mg./1. min. It follows that the decomposed amount of H_2O_2 was about 1/110 as much as the case without the addition.

WHAT WE CLAIM IS:—

1. A method of stabilizing hydrogen peroxide in an acidic aqueous solution of hydrogen peroxide containing copper ion capable of catalytically decomposing hydrogen peroxide, said method comprising adding as stabilizer to said aqueous solution, at least one glycol ether represented by the general formula



wherein R is an alkyl group containing 1 to 4 carbon atoms and n is 1 or 2.

2. A method as claimed in claim 1 wherein said glycol ether is added to said aqueous solution in an amount not less than 0.1 g./l.

3. A method as claimed in claim 1 or 2 wherein said glycol ether is added to said aqueous solution in an amount of from 0.1 g./l. to 5 g./l.

4. A method as claimed in any one of the preceding claims wherein said glycol ether is selected from ethyleneglycol monomethylether, ethyleneglycol monoethylether, ethyleneglycol monobutylether, diethyleneglycol monomethylether, diethyleneglycol monoethylether,

ether, and/or diethyleneglycol monobutyl-ether.

5 5. A method as claimed in any one of the preceding claims wherein said acidic aqueous solution contains a mineral acid.

6. A method as claimed in any one of the preceding claims wherein said acidic aqueous solution contains sulphuric acid, nitric acid and/or phosphoric acid.

10 7. A method of stabilizing hydrogen peroxide in an acidic aqueous solution of hydrogen peroxide containing copper ion capable of catalytically decomposing hydrogen peroxide

as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the foregoing Examples. 15

8. Hydrogen peroxide whenever stabilized by a method as claimed in any one of the preceding claims.

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